1. Ammonium sulfite; $(NH_4)_2SO_3$; [10196-04-0]

2. Water; H₂O; [7732-18-5]

EVALUATOR:

Mary R. Masson, Dept. of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, AB9 2UE, Scotland, UK. March 1984.

CRITICAL EVALUATION:

Three studies have been made of the binary system ammonium sulfite - water (1 -3) and further data are available from studies of ternary systems (3 - 8). Yasuda (1) reported his results as amount-of-substance concentrations, and these cannot be converted to mass % or molality; thus, the data cannot be compared with other work. Yasuda reported that the solid phase in equilibrium with solutions at temperatures from 298 - 333 K (25 - 60°C) was $2(NH_4)_2SO_3.3H_2O$, but this does not seem to be confirmed in any other work; Mellor (9) reports some early work that postulated formation of $(NH_4)_2SO_3.1\frac{1}{3}H_2O$, but says that this was probably imperfectly dried monohydrate.

The other data all say that the solid phase, up to 353.2 K, is the monohydrate, $(NH_4)_2SO_3.H_2O$ [7783-11-1]. Above that, it is the anhydrous salt.

The data of Terres and co-workers (6 - 8) are very imprecise, and they are not in agreement with the other data, so all the points are rejected. The rest of the data are in reasonable agreement, with the exception of a few points, which were rejected before the final regression equations were derived.

The regression equations are (1) for 258.2 - 273.2 K, solid phase = ice

$$(T - 273.15) = -0.0467 - 0.331y - 0.000147y^3$$
 $s = 0.103$ (20 pts)

or

$$y = -0.095 - 3.11(T - 273.2) - 0.0698(T - 273.2)^2$$
 $s = 0.206 (20 pts)$

and (2) for 258.2 - 353.2 K, solid phase = $(NH_A)_2SO_3.H_2O$

$$y = 32.3 + 0.273(T - 273.2) + 0.00000945(T - 273.2)^3$$
 $s = 0.203$ (33 pts)

where y = 100w is the solubility in mass % of $(NH_4)_2SO_3$, T is the temperature in K, and s is the standard deviation of the dependent variable about the regression line.

At temperatures above 354.0 K there is a different solubility line, for the solution in equilibrium with $(NH_4)_2SO_3$, but there were insufficient points available to justify calculation of a smoothing equation.

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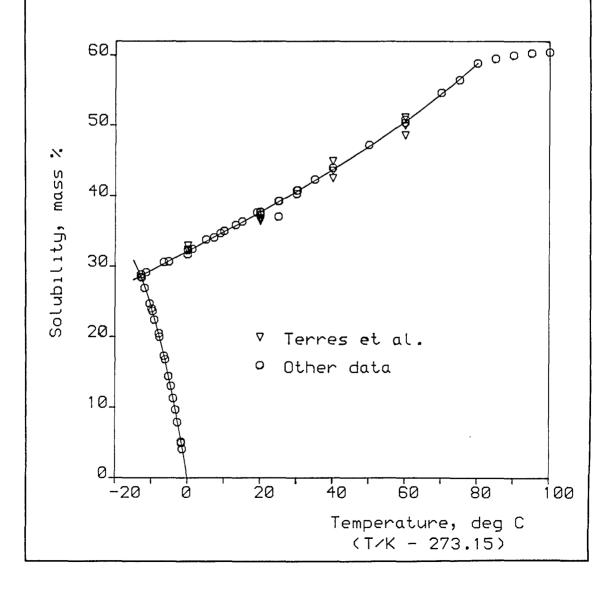
March 1984.

(continued) CRITICAL EVALUATION:

TENTATIVE SOLUBILITIES

The following tentative solubility values for $(\mathrm{NH_4})_2\mathrm{SO}_3$ in water were calculated from the second regression equation.

T/K	Solubility	
	mass %	molality,
		mol/kg
263.2	29.5	3.60
273.2	32.2	4.09
283.2	34.9	4.62
293.2	37.7	5.21
303.2	40.6	5.89
313.2	43.7	6.68
323.2	47.0	7.64
333.2	50.6	8.82
343.2	54.5	10.31
353.2	58.9	12.34



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CRITICAL EVALUATION: (continued)

Ammonium sulfite - ammonia - water. The solubilities measured by Hill (10) for this system are rather lower than those of Ishikawa and Hiroshi (11), despite being measured at the same temperature. The experiments differed in that Hill worked with SO_2 and NH_3 , whereas Ishikawa and Hiroshi used $(NH_4)_2SO_3$ and NH_3 . The trends observed are similar, and there is no clear indication of which results should be preferred; I am inclined to favour those of Ishikawa and Hiroshi, because their work was more directly concerned with measurement of solubilities. The solid phase is the monohydrate $(NH_4)_2SO_3.H_2O$ [7783-11-1].

The results of Terres and Hahn (6) are not in agreement with the other data, except at one or two points. Examination of the data shows it to be highly erratic. Although a small number of the points do appear reasonable, many more obviously contain gross errors. This work is therefore rejected.

<u>Ammonium sulfite - ammonium pyrosulfite - water</u>. This system has also been described in terms of ammonium sulfite - sulfur dioxide - water and ammonium sulfite - ammonium hydrogen sulfite - water: to facilitate comparison, all the data were converted so as to express the system in terms of ammonium sulfite - ammonium pyrosulfite - water.

The results of Vasilenko (3) for 273.2, 293.2 and 303.2 K (0, 20 and 30°C) appear to be in reasonable agreement with those of Ishikawa and Hiroshi (11) for 298.2 K (25°C). The results of Hill (10) for 298.2 K are rather lower - they lie below Vasilenko's 293.2 K line. The results of Terres and Hahn (6) for 293.2 K agree with Vasilenko's data for the same temperature when the ammonium pyrosulfite content is below 15%. At higher pyrosulfite contents, they approach Vasilenko's data for 303 K.

Ammonium sulfite - ammonium sulfate - water. The results of Ishikawa and Murooka (12) at 288.2 and 303.2 K are in good agreement with those of Vasilenko (3) at 283.2 and 293.2 K. The rather limited amount of data provided by Ishikawa and Murooka for higher temperatures also appears to be in agreement with Vasilenko's more detailed work. The data of Terres and Heinsen (8) are in poor agreement with these.

<u>Ammonium sulfite - sodium sulfite - water</u>. Ternary systems (5,13) and more complex ones (13,14) are discussed under sodium sulfite.

Other ternary systems. Ammonium sulfite - ammonium chloride - water (5), and ammonium sulfite - ammonium thiosulfate - water (7) have also been studied.

QUATERNARY SYSTEMS

Two studies of the quaternary system ammonium sulfite - ammonium hydrogen sulfite - ammonium sulfate - water have been described (15,16).

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EVALUATOR:

March 1984.

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CRITICAL EVALUATION: (continued)

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